



Enhanced self-catalytic degradation of CuEDTA in the presence of H₂O₂/UV: Evidence and importance of Cu-peroxide as a photo-active intermediate

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ABSTRACT

A new insight into the degradation of CuEDTA with UV/H₂O₂ was performed. It was found that the degradation was an UV-enhanced self-catalytic process with two main stages. The first was the induction stage in which cupric ions were produced in CuEDTA degradation with UV photolysis or/and H₂O₂ oxidation. The second was the photo-catalytic degradation stage in which CuEDTA was oxidized by UV-enhanced cupric ion-based Fenton process. The degradation efficiency reached as high as 82.2% during 18 min, being 37.4 times higher than the efficiency sum of single H₂O₂ oxidation and single UV photolysis. The enhancement effect can be contributed to the synergetic interaction between H₂O₂, cupric ion and UV, specially, to the excellent photo-activity of copper-peroxide intermediates. One of them was identified to be CuO₂ by analysis of its CE-C⁴D electropherograms, UV-vis adsorption spectra, FT-IR spectra, Raman spectra, especially XPS spectra. The enhancement mechanism was experimentally confirmed to be due to the acceleration of Cu(II)-to-Cu(I) transform by the photolysis of copper-peroxide intermediates, leading to the increasing CuEDTA degradation.

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1. Introduction

Organic chelating agents, such as ethylenediaminetetraacetic acid (EDTA), nitrilotriacetic acid (NTA), diethylenetriaminepentaacetic acid (DTPA) and so on, and their metal complexes has been extensively used in the electroplating, textile, nuclear industries and chemical cleaning processes [1,2]. For example, it has been estimated that about 65,000 t of EDTA and DTPA-containing complexes are used a year [3]. These complexes may carry not only toxic metals but also recalcitrant chelating legends into environment. Thus, there is an intensive concern about these composite pollutants.

In them, CuEDTA is one of most frequently used metal chelated complexes [4,5]. Its strong complexing nature causes difficulty in the related effluent treatment. For example, the cupric ion in CuEDTA can't be efficiently removed from wastewater by conventional methods of chemical precipitation including OH⁻, S²⁻, CO₃²⁻ etc. [6,7]. Generally, a two-step strategy, pre-oxidation for EDTA and post-precipitation for cupric ion, is becoming a particu-

larly attractive alternative for the removal of both cupric ions and organic pollutants from wastewater [8–10].

Recently, some advanced oxidation processes (AOPs) as the pre-oxidation technologies have been used to treat CuEDTA-containing wastewater, due to their high oxidative power and unselective reactive nature. These AOPs include Fenton and photocatalytic oxidation etc. [1,2,11–14]. They could efficiently degrade CuEDTA, even mineralize it into CO₂, other simple inorganic ions, leading to generation of free cupric ions. For example, Yang and Davis investigated the percentage distribution of copper(II) species in TiO₂-mediated photocatalytic degradation of CuEDTA and found that 60% coordinated copper was turned to free cupric ions after a 60-min photocatalytic oxidation at pH 4 [11].

It is well known that free cupric ions are also catalysts of H₂O₂-based AOPs [15,16]. Therefore, it can be expected that the free cupric ions, as a kind of CuEDTA degradation products, will possibly catalyze H₂O₂ to degrade CuEDTA by Fenton-like mechanism (1–4) [17]. This kind of catalytic reaction using its products as catalysts is generally called self-catalysis [18,19]. In the view of 'green chemistry', it is an interesting topic to understand the self-catalytic performance of cupric ions, as a component of pollutants, not an

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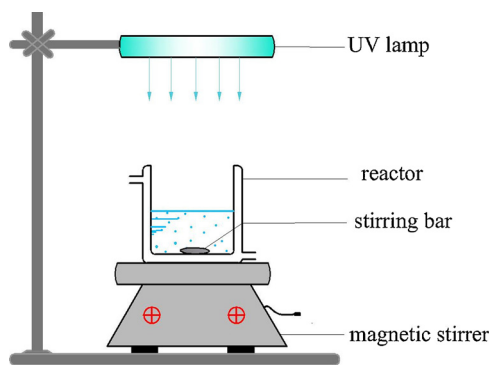
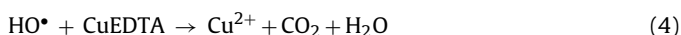
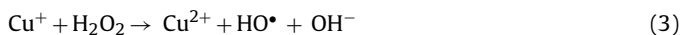
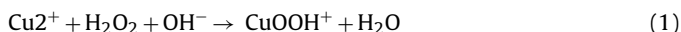


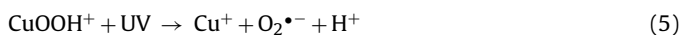
Fig. 1. Schematic diagram of UV photo-reactor.

additional catalyst, in the degradation of copper-containing pollutants in wastewater.



The combination of hydrogen peroxide with ultraviolet light ($\text{H}_2\text{O}_2/\text{UV}$) is a kind of typical AOPs and has been used in the degradation of organic pollutants including complex agents [20–22]. However, so far, little information about the degradation of CuEDTA by $\text{H}_2\text{O}_2/\text{UV}$ is available [23].

According to J.F. Perez-Benito's investigation [17], the Reaction (2) is the determining rate step. Thus, if Cu-peroxides in the Reaction (2) possess photo-reduction activity, UV light may promote the CuOOH⁺ decomposition by Reaction (5), resulting in the increase of self-catalytic degradation rate for CuEDTA.



This issue attracts our interest in approaching to the degradation of CuEDTA by $\text{H}_2\text{O}_2/\text{UV}$. The present work will focus on the investigations on the occurrence, characteristics and effect of the enhanced self-catalysis. A special attention will be paid to the evidence and importance of Cu-peroxide as a photo-active intermediate. The aim of this work is to understand well the mechanism of the enhanced self-catalytic degradation of copper-containing pollutants with $\text{H}_2\text{O}_2/\text{UV}$.

2. Experimental

2.1. Reagents and chemicals

EDTA was purchased from Tianjin Baishi Chemical Reagent Co., Ltd. (China). CuCl_2 was bought from Tianjin Fuchen Chemical Reagent Co., Ltd. (China). H_2O_2 was obtained from Guangzhou Chemical Reagent Industries (China). Ferricytochrome C and bathocuproine (BC) were purchased from Aladdin Chemistry Co., Ltd. All reagents used were of analytical grades unless otherwise stated.

Ultrapure water through the study was obtained by HJJ-ROEDI-HM-B-100 of Guangzhou Jingyuan Desalination and Water Treatment Co., Ltd. (China). All stock solutions were kept in a refrigerator at 4 °C. Solutions of CuEDTA were prepared by mixing a solution of CuCl_2 and EDTA at a molar ratio of 1:1. Running solutions were prepared fresh daily by diluting stock solutions.

2.2. Determination and characterization

The concentrations of CuEDTA, EDTA, and AO II (acid orange II), were determined by CE-C⁴D (capillary electrophoresis with capacitively coupled contactless conductivity detection) [24,25], was manufactured by School of Chemistry and Chemical Engineering, Sun Yat-sen University, China [26]. The total organic carbon (TOC) was detected by a TOC analyzer (Shimadzu, Japan). Cu^+ concentration was quantified spectrophotometrically using bathocuproine (BC) as the color forming reagent [27]. Upon addition of BC, Cu^+ rapidly formed a $\text{Cu}(\text{BC})_2$ complex which was measured colorimetrically at 484 nm. EDTA was added to the BC solution to bind Cu^{2+} , preventing any BC induced reduction of Cu^{2+} . Ferricytochrome C reduction was used to assess superoxide anion ($\text{O}_2^{\bullet-}$) production [28]. The absorbance of the medium was read spectrophotometrically at 530 nm against distilled water blank. Reduction of ferricytochrome C in the presence of $\text{O}_2^{\bullet-}$ was subtracted from the values without it. The concentration of H_2O_2 was quantified spectrophotometrically by the KI dosimetry method [29]. UV/vis absorption spectrum was scanned by a UV-vis spectrophotometer (UV-2700, Shimadzu). The concentration of *p*-chlorophenol was analyzed by the high performance liquid chromatography (HPLC, LC15, Shimadzu, Japan) with a UV detector (SPD-15 C) at 280 nm. The mobile phase was a filtered solution of 70/30 (v/v) methanol–water with a flow rate of 1 mL/min.

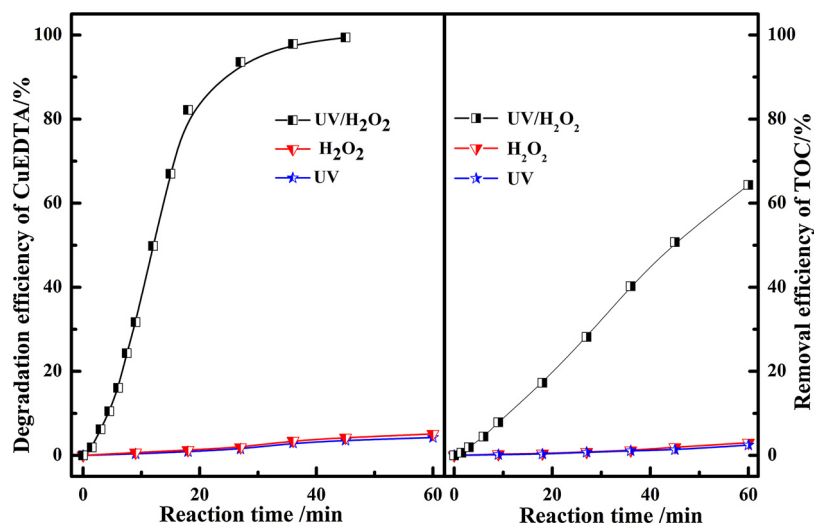


Fig. 2. Degradation efficiency (left) and TOC removal efficiency (right) of CuEDTA (1.2 mmol L^{-1}) by H_2O_2 (120 mmol L^{-1}), UV (6 W) or $\text{H}_2\text{O}_2/\text{UV}$.

The FT-IR spectra of the samples were recorded using Thermo Scientific model iS50 FT-IR instrument. X-ray photoelectron spectroscopy (XPS) analyses were carried out on an ESCALAB 250 photoelectron spectrometer (Thermo-VG Scientific). Raman spectra were measured using a Fourier Transform Raman (FT-Raman) Spectrometer (Nicolet NXR 9650, Thermo-Fisher, USA) equipped with a green laser of 514 nm.

2.3. Experiment procedures

Degradation experiment was performed in a photo-reactor (Fig. 1) with Philips low pressure UV lamps (6W, 254 nm). The water samples were placed in an open reactor (90 × 15 mm) beneath the UV lamps, and the path length of the light in the solution was 25 cm. Samples were taken at a given time interval from the reactor to detect. The system was equipped with a stirrer to achieve good mixing throughout the experiment.

The precipitation was acquired by centrifugal separation (TDZ5-WS centrifugal machine, Xiangyi) and then vacuum drying in vacuum freeze dryer (Labconco).

3. Results and discussion

3.1. Enhanced self-catalytic degradation of CuEDTA in the presence of H₂O₂/UV

Degradation of CuEDTA in the presence of H₂O₂ and UV can be simply resolved into three potential processes: UV photolysis, H₂O₂ oxidation and H₂O₂/UV combining oxidation. In order to understand the contribution of each process, the left of Fig. 2 presents the degradation efficiency as the time function in the three processes. It can be seen clearly from the figure that the combination process of UV and H₂O₂ can degrade CuEDTA much more than the single H₂O₂ oxidation or UV photolysis. For example, for 18 min, the degradation efficiency of CuEDTA by H₂O₂/UV reaches as high as 82.2% while that of CuEDTA by single H₂O₂ oxidation or UV photolysis is only 1.3% and 0.9%, respectively. The former is 63.2 and 91.3 times of the latter, correspondingly. Although the removal efficiency of TOC is just 64.3% for a 60-min H₂O₂/UV reaction, apparently less than that of CuEDTA, the removal efficiency of TOC for the H₂O₂/UV process

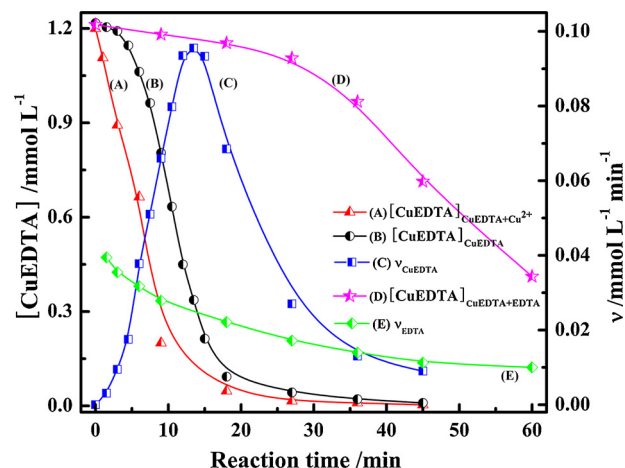


Fig. 3. Changes of concentration and rates in the degradation of CuEDTA (1.2 mmol L⁻¹) and EDTA (1.2 mmol L⁻¹) by UV (6 W)/H₂O₂ (120 mmol L⁻¹), (v was degradation rate obtained by the continuously differentiable calculation in Origin Pro. 7.5).

is also much higher than that of single H₂O₂ oxidation (3.1%) and UV photolysis (2.4%) during 60 min, as shown in the right of Fig. 2. These facts indicate that the contribution of the single H₂O₂ oxidation or UV photolysis of CuEDTA can be neglected. Therefore, the following investigation will focus on the contribution of H₂O₂/UV combining process to the degradation of CuEDTA.

Fig. 3 presents the changes of concentration and degradation rates of CuEDTA. It is noticed that the CuEDTA concentration vs time curve (curve B) shows a similar 'S-like' appearance and the degradation rate vs. time curve (curve C) is a bell-shaped look. These features are consistent with that of self-catalytic reaction [30,31]. In the both curves, the slow degradation is the induction stage of the process and the fast degradation is the self-catalytic stage. The length of the induction stage is dependent on the ratio of EDTA and cupric ion. The greater the ratio is, the longer the induction stage is. As shown in Fig. 3, almost no induction stage is observed for the reaction system with exceed cupric ions (curve A). The induction stage for the ratio with 1, e.g., CuEDTA, is about 3 min (curve

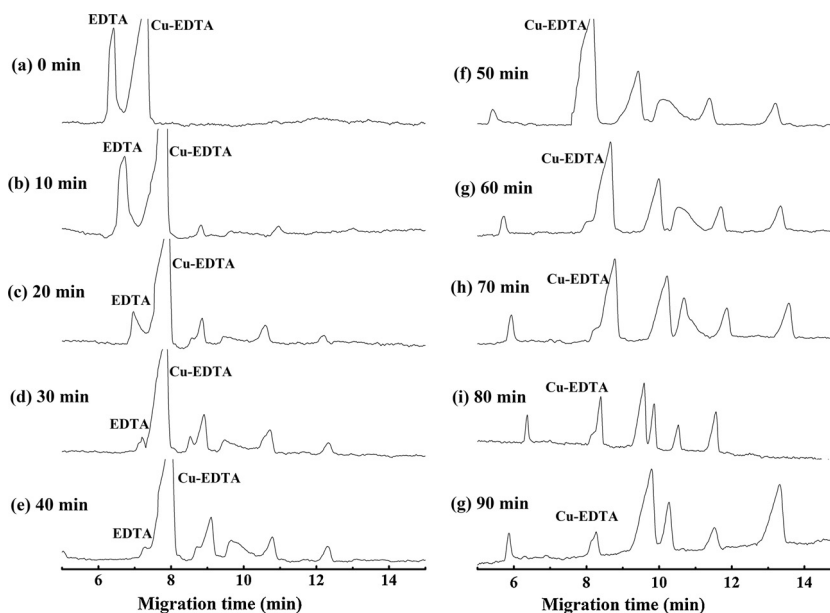


Fig. 4. CE-C⁴D electropherograms for CuEDTA + 0.5EDTA at different degradation time by H₂O₂/UV (determining conditions: 20 mmol L⁻¹ acetic acid solution and applied voltage 15 kV).

B), and that of the ratio with 1.5 increases to about 30 min (curve D), showing more obvious characteristics of self-catalytic reaction. This is because that it takes more time to degrade exceeded EDTA firstly, as shown in the CE-C⁴D electropherograms (Fig. 4).

In order to understand the self-catalytic process, curve E of Fig. 3 also presents the degradation rate (ν_{EDTA}) of single EDTA with time in the presence of H₂O₂/UV. It can be seen from the figure that ν_{CuEDTA} is apparently less than ν_{EDTA} before the first 3 min, however, becomes greater than ν_{EDTA} after the first 3 min. For 30 min, CuEDTA almost is degraded completely. The difference before the first 3 min is consistent with J.A. Frim et al's report, in which the coordinated copper has been found to inhibit the degradation of EDTA without illumination [32]. The difference after the first 3 min can be possible dependant on UV-enhanced self-catalytic effect of cupric ions released with degradation of CuEDTA by H₂O₂/UV, because no self-catalytic enhancement effect is observed for EDTA-H₂O₂/UV system, e.g., without copper system, as shown in the curve (E) of Fig. 3, although the degradation efficiency is increased, comparing with single UV photolysis or H₂O₂ oxidation.

3.2. Evidence of Cu-peroxide complex as a photo-active intermediate

The photo-picture of Fig. 5 presents the color changes of CuEDTA solution with time in the process of H₂O₂/UV oxidation. It can be observed that the pale blue firstly changes to yellow-blue, then to yellow at about 30 min and finally returns to pale blue after 480 min. The yellow disappearance coincides with the exhaust of H₂O₂, as shown the insert of Fig. 5. However, no yellow intermediate is observed for EDTA-H₂O₂/UV system. These facts suggests that the yellow intermediate is dependent on copper and H₂O₂.

The absorbance spectral changes of CuEDTA solution with time are also shown in Fig. 5. A shoulder peak is observed at about 350–400 nm and slowly increases with reaction time. The position and morphology of the shoulder peak is similar to those of Cu-peroxide complexes with side-on binding mode [33–37]. These facts suggest that the yellow intermediate is possibly a kind of Cu-peroxide compound. These shoulder peaks can be assigned to a —O—O— → Cu(II) ligand-to-metal charge transfer (LMCT) transition in the Cu-peroxide complexes [38,39].

In order to further confirm the suggestion, the reaction of CuCl₂ and H₂O₂ in the absent of organic ligand is investigated. When CuCl₂ and H₂O₂ are mixed, a yellow compound apparently appears at above pH 4.96, but no yellow compound is observed below the pH

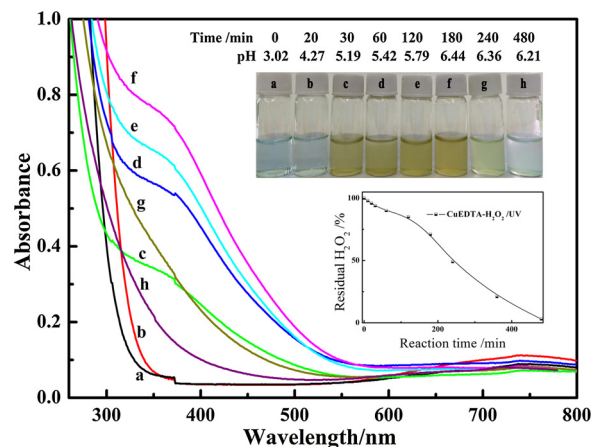


Fig. 5. Changes of color and UV/vis absorption spectra in the degradation of CuEDTA (1.2 mmol L⁻¹) by UV (6 W)/H₂O₂ (Inset: the change of residual H₂O₂ in the degradation).

value, as shown in Fig. 6(A). The rising pH value is beneficial to the formation of the yellow compound. The fact indicates that the formation of the yellow compound is dependent on the deprotonating process of H₂O₂.

Parallel to formation of the yellow compound, a shoulder peak appears at about 350–400 nm in the absorption spectrum of the reaction solution. The absorption spectrum is much similar to that of the yellow copper-peroxide intermediate in the UV/H₂O₂ degradation of CuEDTA. The yellow compound can be separated from the solution as a kind of precipitate, as shown in the photo-picture of Fig. 6(B). In its FT-IR spectrum of Fig. 6 (B), a characteristic peak at 1106 cm⁻¹ is clearly observed. The characteristic is consistent with the stretching vibration of the —O—O— bond in copper-peroxide compound [40–42]. In its Raman spectrum of Fig. 6(C), there are two main peaks, one is positioned at 829 cm⁻¹, and the other is located at 558 cm⁻¹. The former is located in the Raman shift range of the —O—O— bond stretching vibration and the latter is much close to Raman shift of the Cu—O stretching vibration. The result further confirms that the yellow precipitate is a kind of copper-peroxide compound.

The left of Fig. 7 shows that XPS peak of O1s appears at 531.35 eV. The binding energy is higher than that (529.9 eV) of O1s in CuO, but much similar to that (531.1 eV) of O1s in strontium peroxide

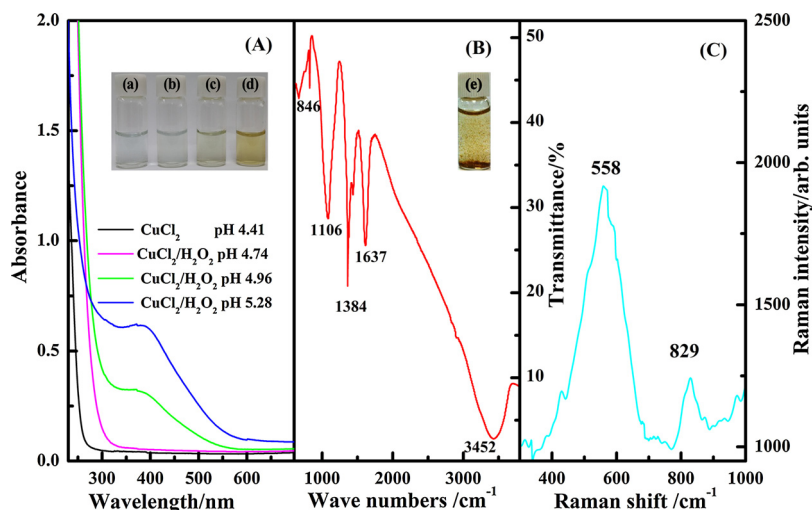


Fig. 6. (A) Changes of color and UV/vis absorption spectra of the mixing CuCl₂ (1.2 mmol L⁻¹)/H₂O₂ (120 mmol L⁻¹) at different pH; (B) FT-IR spectrum of the yellow precipitate; (C) Raman spectrum of the yellow precipitate.

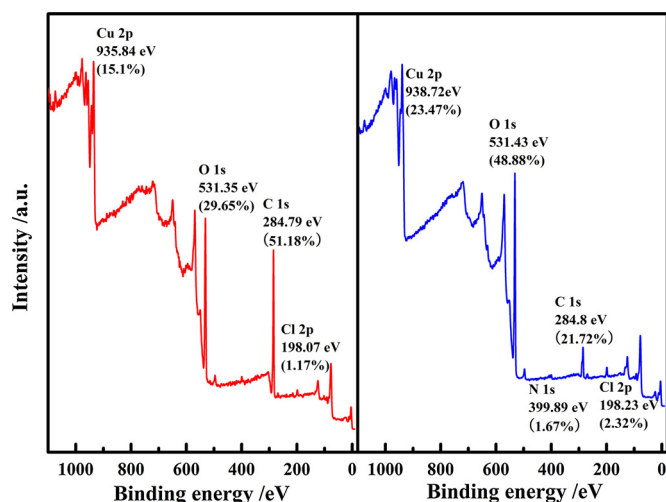


Fig. 7. XPS spectra of yellow precipitations (left: from $\text{CuCl}_2\text{-H}_2\text{O}_2$ system with pH 6, right: from $\text{CuEDTA-H}_2\text{O}_2/\text{UV}$ system after 120 min).

Table 1

Degradation difference of three typical pollutants (0.12 mmol/L, 20 mL) by UV photolysis, CuO_2 (5 mg) oxidation and CuO_2 (5 mg)/UV oxidation for 2 h and $2 \times 6 \text{ W UV}$ light.

Degradation processes	Degradation efficiency (%)		
	EDTA	AO II	<i>p</i> -Chlorophenol
UV	2.2	3.5	69.2
CuO_2	20.62	18.4	23.9
CuO_2/UV	48.4	50.0	96.1

(BaO_2), further confirming that the yellow compound is a kind of copper-peroxide [43]. At the same time, it can be observed from the XPS figure that the atom ratio of oxygen and copper is close to 2 while that of chlorine and copper is only 0.07, indicating that chlorine atom can be almost neglected and the yellow compound is mainly CuO_2 . The right of Fig. 7 is the XPS spectrum of the yellow precipitation obtained from $\text{CuEDTA-H}_2\text{O}_2/\text{UV}$ reaction system. It is much close to the left XPS spectrum of Fig. 7, except a little of nitrogen element. Specially, the atom ratio of O/Cu and the binding energy of Cu2p and O1s are almost identical with these of the left. These facts suggest the yellow precipitation from the $\text{CuCl}_2\text{-H}_2\text{O}_2$ and $\text{CuEDTA-H}_2\text{O}_2/\text{UV}$ system are both CuO_2 .

Table 1 shows the degradation efficiency of three typical organic pollutants, EDTA, AO II and *p*-chlorophenol by direct UV photolysis, CuO_2 oxidation and their combining process (CuO_2/UV), respectively. It can be seen from the figure that these pollutants can be degraded by these three processes, but the degradation efficiency of the combining process is apparently higher than that of single UV photolysis or CuO_2 oxidation. For example, for 120-min degradation, the efficiency of CuO_2/UV for AO II is 50.0%, higher than that of single UV photolysis (3.5%) or CuO_2 oxidation (18.4%). These results show that CuO_2 possesses a favorable UV photo-activity. This is also based on the UV-enhanced self-catalytic effect in CuEDTA degradation with $\text{H}_2\text{O}_2/\text{UV}$.

3.3. Enhanced self-catalytic pathway of CuEDTA degradation with $\text{H}_2\text{O}_2/\text{UV}$

Although no information about the degradation mechanism of CuEDTA with $\text{H}_2\text{O}_2/\text{UV}$ is available up to today, there are possible three key intermediates, $\cdot\text{OH}^-$, Cu^+ and $\text{O}_2^{\cdot-}$ at least, in addition to the mentioned CuO_2 , according to the typical Cu-based Fenton mechanism [17]. In them, the occurrence of $\cdot\text{OH}^-$ in the cupric ion-

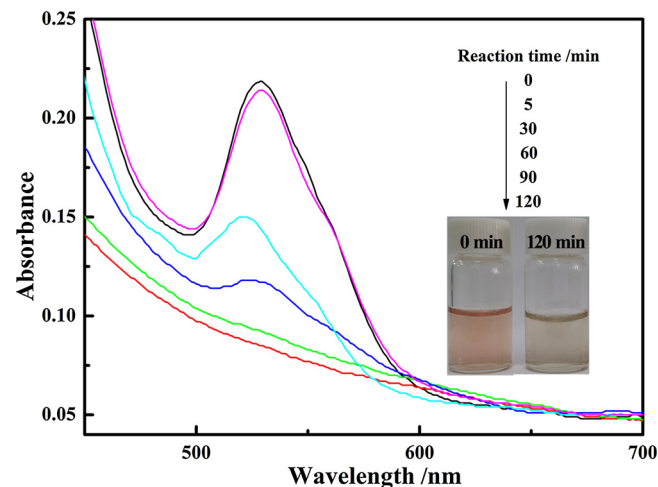


Fig. 8. Changes of UV/vis spectra for ferricytochrome C added the solution from $\text{CuEDTA-H}_2\text{O}_2/\text{UV}$ for various reaction times.

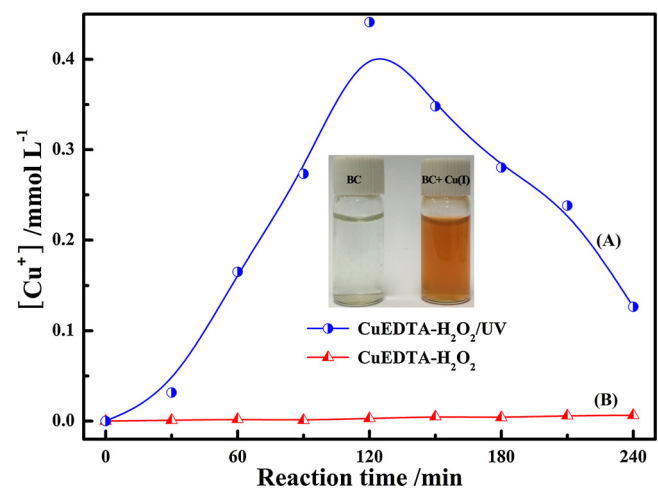


Fig. 9. Concentration of Cu^+ in degradation of CuEDTA with (A) H_2O_2 and (B) $\text{H}_2\text{O}_2/\text{UV}$.

H_2O_2 system has been reported [44] and the following attention is mainly paid to other two intermediates.

The ferricytochrome C is chosen as a probe for $\text{O}_2^{\cdot-}$. It can be seen from Fig. 8 that its absorbance peak at 530 nm decreases and finally disappears, when the illuminated $\text{CuEDTA-H}_2\text{O}_2$ solution for various times is added in the ferricytochrome C solution. Parallel to the decrease, its color changes from pink to colorless, as the insert of Fig. 8. The change of color and absorbance peak suggests the occurrence of $\text{O}_2^{\cdot-}$ in the both systems.

The insert of Fig. 9 shows that the $\text{CuEDTA-H}_2\text{O}_2$ solution after illumination changes into red when BC is added in the solution. The appearance of red color suggests that the occurrence of cuprous ions in the solution because BC is a well-known color forming reagent of cuprous ion. The occurrence of cuprous ions in the solution is consistent with hypothesize [17]. Fig. 9 also presents that concentration of cuprous ion in the degradation of CuEDTA with H_2O_2 and $\text{H}_2\text{O}_2/\text{UV}$, respectively. It can be seen that the concentrations of cuprous ion under UV illumination are apparently higher than that without UV illumination. These facts clearly indicate the UV light can promote the transform of CuO_2 species to cuprous ion and the generation of superoxide radical as illustrated in Reaction (6).



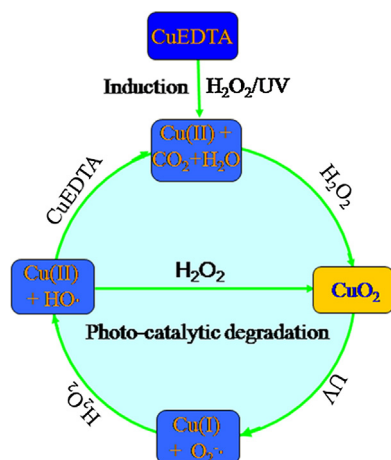


Fig. 10. Enhanced self-catalytic pathway of CuEDTA degradation with $\text{H}_2\text{O}_2/\text{UV}$.

As we known, the transform of cupric ion to cuprous ion is the determining rate step of Cu-based Fenton reaction [17], therefore, it can be inferred that the enhancement effect of UV light on cupric self-catalysis is dependent on the acceleration of $\text{Cu(II)} \rightarrow \text{Cu(I)}$ transform, that is, the photo-reduction of CuO_2 .

It is worth noticing that the enhancement effect of UV is also observed, before the appearance of the yellow CuO_2 , as shown in Fig. 1. The fact suggests that there are possibly some other UV photo-active intermediates. According to the mechanisms of typical copper-based Fenton Reactions (1) and (2) [17], the photo-active intermediates may be CuOOH^+ -containing compounds, although these intermediates have not been separated from $\text{CuEDTA-H}_2\text{O}_2/\text{UV}$ system till now. Certainly, it is much difficult to separate them from the solution, because these CuOOH^+ -containing compounds with end-on binding mode is generally thermodynamically unstable [45,46].

Combining the reported cupric-based Fenton mechanism (1–6) [17] with above experimental observation, specially the finding of photo-active CuO_2 and the confirm of intermediates, Cu^+ , $\text{O}_2^{\bullet-}$ in $\text{CuEDTA-H}_2\text{O}_2/\text{UV}$ system, a simple enhanced self-catalytic pathway for the oxidation of CuEDTA with $\text{H}_2\text{O}_2/\text{UV}$ can be suggested below (Fig. 10).

4. Conclusions

The degradation process of CuEDTA with $\text{H}_2\text{O}_2/\text{UV}$ is characterized with a self-catalytic reaction. The degradation efficiency for $\text{H}_2\text{O}_2/\text{UV}$ combining process is much higher than the efficiency sum of single H_2O_2 oxidation and single UV photolysis. The enhancement effect can be contributed to the synergetic interaction between the H_2O_2 , cupric ion and UV, specially, to the excellent photo-activity of copper-peroxide intermediates. One of these intermediate was experimentally identified to be CuO_2 . The enhancement mechanism is experimentally confirmed to be due to speeding up the determining rate step of Cu-based Fenton, that is, the reduction of cupric ion to cuprous ion by its photolysis, leading to increasing degradation of CuEDTA. Expectedly, the analogous enhancement effect will exist in the degradation of copper-based complexes with $\text{H}_2\text{O}_2/\text{UV}$.

Acknowledgments

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